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Diallyl Phthalate Plastic Molding Resins  
and Molded Parts**

**Ruth B. Whitaker, Jerome E. Glaub,  
Nicholas R. Bonekowski and Philip D. Gillham**

**December 1, 1980**

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**Issued: December 1, 1980**

**★ Monsanto Company, St. Louis , Physical Sciences Center**

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# Abstract

Characterization of diallyl phthalate (DAP) molding resins was undertaken by differential scanning calorimetry (DSC) and by combined size exclusion chromatography (SEC)/low angle laser light scattering (LALLS) in order to better predict moldability and storage life limits. Completeness of cure of molded parts, before and after any "post-curing," was also determined by thermal analysis.

Molecular weights and molecular weight distributions of the DAP molding resins by SEC/LALLS indicated that the "better" molding resins have lower  $M_w/M_n$  ratios. Association effects were observed, which could not be overcome by solvent modification alone. Determination of DAP molding resin heats of reaction by DSC indicated a linear relation between  $\Delta H_R$  and weight percent filler for the "good" molding resins.

DSC analyses of molded DAP parts showed that 95% cure was achieved in some as-molded parts, with a post-cure temperature of 165°C being required to complete the cure to 100%. Thickness of the parts was a factor, with the thicker parts being 100% cured as molded. The glass transition temperature ( $T_g$ ) of the molded parts increased as cure was completed, to ~160-165°C maximum. These results are consistent with a model of thermoset resin curing behavior which states that 100% cure can be achieved only if a post-curing operation is conducted above the  $T_{g\infty}$  ( $T_g$  at complete cure) of the polymer.

## 1. Introduction

Characterization of diallyl phthalate (DAP) molding resins and molded parts was undertaken (1) to avoid previous problems encountered with vendor-supplied, fiber-glass-filled, plastic molding resins and (2) to improve plastic products. Thermal analytical techniques and gel permeation chromatography (GPC) were used. The prime objectives were to develop more meaningful acceptance criteria, in relation to moldability, for vendor-supplied DAP molding resins and to set realistic storage life limits for them. It was envisioned that these methods could also be applied to glass-filled DAP molding resins produced later in-house, and to other filled resin materials.

### 1.1. DAP polymerization

Some description of the DAP polymerization process, and its possible effect on moldability and molded part properties, is essential to any discussion of characterization techniques and results. All molding resins studied here, insofar as is known, were based on the *o*-DAP monomer. In polymerizing *o*-DAP two types of products, shown in Figure 1, may be formed, along with mixtures combining the two structures. Of particular importance is the formation of cyclic structures (Type 1) which have been found to comprise up to 40% of the total *o*-DAP prepolymer at the gel point (~26% conversion) [1]. From the standpoints of both moldability and final physical properties, it is probably more desirable to

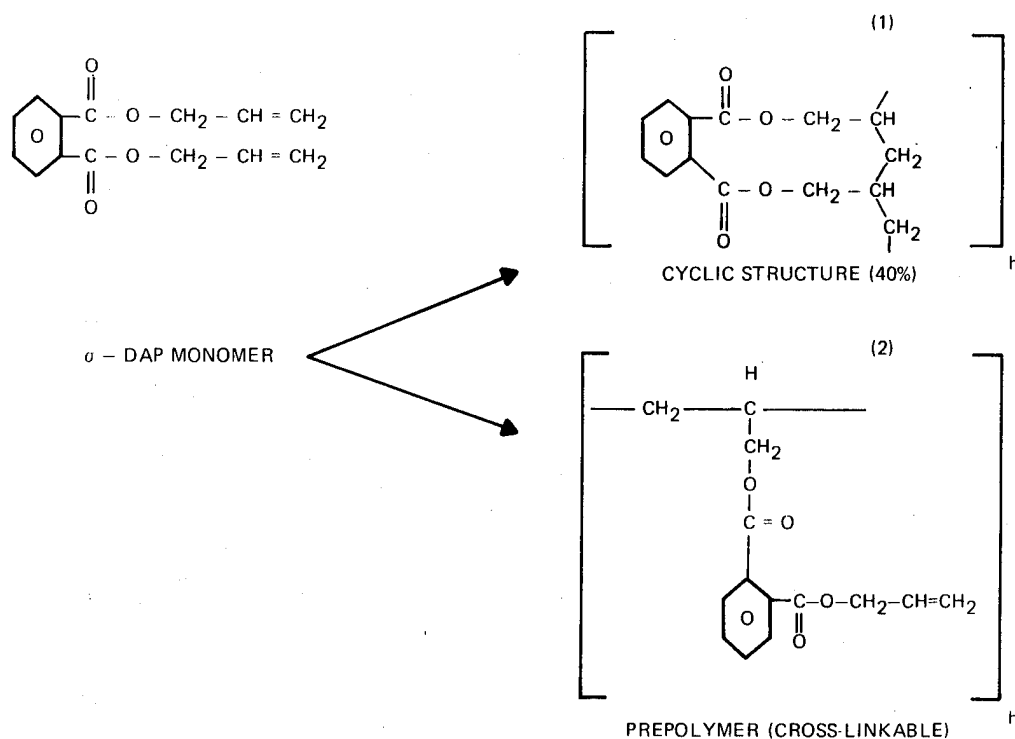
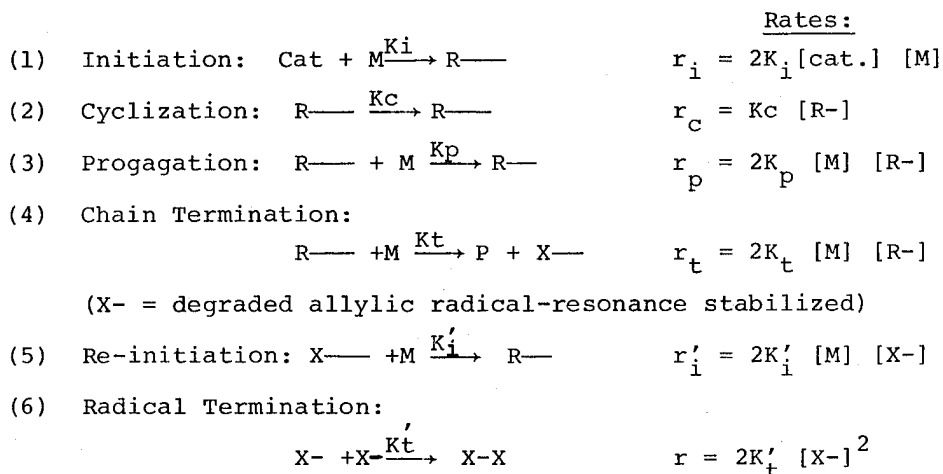


FIGURE 1 - DAP polymerization.

have predominantly the crosslinkable Type 2 structure. The Type 1 structure obviously cannot participate either in reactions with the vinyl alkoxy silanes typically used to coat fiberglass to promote resin adhesion, or in any crosslinking reactions on molding of the fiberglass filled resins. Physical properties of molded parts will also be adversely affected, due to reduction in the amount of network structure formation.

## 1.2. Complexity of DAP molding resins

Another factor of importance, particularly in regard to aging on storage of DAP molding resins, is the presence of the terminal allyl group in the cross-linkable prepolymer. The allyl group is resonance stabilized, but may be subject to reinitiation according to the following proposed o-DAP reaction scheme [2]:



OVERALL RATE OF POLYMER FORMATION:

$$R_p = \frac{2 K_p [\text{M}]}{K_t} \cdot \left\{ K_i [\text{cat.}] + K'_i \left( \frac{K'_i [\text{cat}] [\text{M}]}{K'_t} \right)^{1/2} \right\}$$

By itself, the commonly used *o*-DAP prepolymer (Dapon 35, FMC Corp.) would be relatively stable. However, the DAP molding resins are complex mixtures, containing among other constituents added monomer and catalyst, as shown in Table 1. Therefore, they would be subject to the type of re-initiation in the previously shown reaction scheme and must be kept refrigerated to extend storage life. An inhibitor, such as hydroquinone, also is generally added to the commercial molding resins.

Thus, both the nature of *o*-DAP polymerization and the complexity of the DAP molding resins serve to make their characterization difficult. However, some useful insights into both moldability and storage life limits of the molding resins, as well as properties of the molded parts, were expected to be gained through appropriate analyses. This report will describe in detail the results of the GPC and thermal analyses of the DAP molding resins and molded parts to date, and will include recommendations for continuation of the work.

Table 1 - ANALYSIS OF A TYPICAL  
DAP MOLDING COMPOUND<sup>a</sup>

Component	wt %
DAP prepolymer	37.0
Catalyst <sup>b</sup> /DAP monomer	8.2
Cl/Sb <sub>2</sub> O <sub>3</sub> (flame retardants)	5.4
ZnO (from Zn stearate mold release)	0.2
Filler (glass, asbestos, etc.)	49.0

<sup>a</sup>Ref. 3.

<sup>b</sup>Such as *t*-butyl per-benzoate, *t*-butyl peroxide, dicumyl peroxide.

The description of experimental methods used and the results obtained will be divided into two sections: Characterization of molding resins (Section 2); and Analysis of molded parts (Section 3). The molding resins studied included those used in the production of the molded parts, as well as a number of others not selected for production. The molded parts and molding resins are identified according to the program number for which their use was intended.

## 2. Characterization of glass-filled DAP molding resins

The principal methods used to characterize the vendor-supplied, glass-filled DAP molding resins were differential scanning calorimetry (DSC), to determine heats of reaction, and GPC or, more correctly, size exclusion chromatography (SEC), which was used combined with low angle laser light scattering (LALLS), to determine molecular weight distributions. In addition, the routine chemical and physical tests that are normally conducted by Mound's analytical laboratories for resin certification were performed on these resins, and any relevant results are included here. Moldability tests were also performed on these resins, as appropriate to the parts for which they were intended. These were done by established Mound procedures for acceptance/rejection of molded parts, under direction of Manufacturing Development. Again, relevant results will be cited, but no detailed descriptions given here.

### 2.1. Characterization by SEC/LALLS

The molecular weight distributions of several of the glass-filled DAP molding resins were determined at Monsanto's Physical Sciences Center in St. Louis, where the appropriate instrumentation is available, by combined SEC/LALLS.

#### 2.1.1. EXPERIMENTAL

The instrument used was a Chromatix KMX-6 LALLS photometer. Both the DuPont Zorbax<sup>®</sup> bimodal silanized SEC column set and the  $10^6$ ,  $10^5$ ,  $10^4$ ,  $10^3$  Å  $\mu$ strygel<sup>®</sup> GPC column set were examined. Work was completed on

the DuPont columns, which permit a much faster analysis time without sacrificing overall resolution. Tetrahydrofuran (THF)/0.05 wt % maleic acid was used as the mobile phase. The maleic acid was added to eliminate solute adsorption.

Since the DAP molding resins all contained  $\geq 50\%$  filler, the polymer was isolated from the inorganic matrix by three extractions with THF, and then centrifuging and filtering the solution through 0.45  $\mu$  Fluoropore filters. The THF was evaporated off at room temperature. Sample QC-23333 was rendered only partially soluble (on two separate attempts) when treated in this manner. Because of the partial solubility, QC-23333 was not analyzed. The color pigment was difficult to remove completely. Some color remained in the dried resin even after three filtrations.

#### 2.1.2. RESULTS

The complete molecular weight and molecular weight distribution results obtained for all resins evaluated are given in Table 2, and a typical SEC/LALLS chromatogram is shown in Figure 2. A discussion of these results, and the reasons for designating these molecular weights as only "apparent" molecular weights follows.

A bimodal type distribution (see Figure 2) for these polymers was observed when the initial analysis was done in THF/maleic acid. Association was suspected as a likely cause for this observation. Resin sample QC-23553 was randomly chosen and studied in five different solvent systems, with and without solvent modifiers, in an effort to overcome the association effects. The results obtained in those various solvent systems are shown in Table 3.

Table 2 - RESULTS OF SEC/LALLS ANALYSIS OF GLASS-FILLED DAP MOLDING RESINS

DAP Resin		Apparent Molecular Weights			Molecular Weight Distribution	
Program	Resin QC No.	$M_w$	$M_n$	$M_z$	$M_w/M_n$	$M_z/M_n$
A	QC-23321 (repeat)	256,600	55,200	1,210,000	4.65	22
		251,000	61,700	1,170,000	4.06	19
A	QC-23322 (repeat)	293,700	185,600	830,000	1.58	4.5
		292,200	189,800	1,300,000	1.54	6.8
A	QC-23333	No data obtainable due to resin insolubility				
B	QC-23396 (repeat)	199,300	20,800	786,000	9.57	38
		195,700	22,500	927,000	8.69	41
C	QC-23553 (repeat)	352,600	33,200	4,000,000	10.6	120
		336,700	37,800	3,100,000	8.9	82
D	QC-23531	399,300	21,600	4,150,000	18.5	192
E	(repeat)	396,200	18,700	3,500,000	20.1	177

The bimodal character was present in all solvent systems tested except hexafluoroisopropanol (HFIP). In HFIP only the higher molecular weight peak (leading peak) of the SEC curve was present; the lower portion had disappeared. The lower molecular weight peak was most pronounced in the methyl ethyl ketone (MEK) solvent system. Except for MEK, the data indicate that 1) increasing the polarity of the solvent system increases the degree of association and 2) the apparent molecular weight increases. The data suggest that using a solvent with a polarity index lower than that of THF would help in reducing association. Unfortunately, other solvents tested with polarity much less than THF became non-solvents for the polymer. In no case could the higher molecular weight associated fraction be eliminated by modifying the polarity of the solvation medium. The tendency for the diallylphthalate species to associate with either solvent or itself is apparently so strong that it cannot be overcome through solvent modification alone. Therefore, the molecular weights reported here are apparent values and not the true molecular weights.

Even though it was not possible to obtain true or absolute molecular weight measurements on the diallyl phthalate molding resins studied, nevertheless, these results were useful for comparative evaluations. They could not, unfortunately, be employed as quantitative standards for calibration for GPC analysis of other DAP molding resins at Mound, as had been planned initially.

It was of interest, though, to compare the molecular weight distributions obtained by SEC/LALLS with the relative ease of molding ("moldability") of these DAP resins for the molded parts for which they were intended. This comparative analysis is given in Table 4. Although the number of samples for which molecular weight distribution data are available is not large, there is a trend apparent in these results. For the Program A spacer (a relatively "difficult-to-mold" part), the resin having the lowest  $M_w/M_n$  (1.6) and  $M_z/M_n$  (5.7) ratios gave the best results on moldability testing and was selected for production by transfer molding. Another DAP resin having a slightly higher (but still relatively low)  $M_w/M_n$  ratio (4.3)

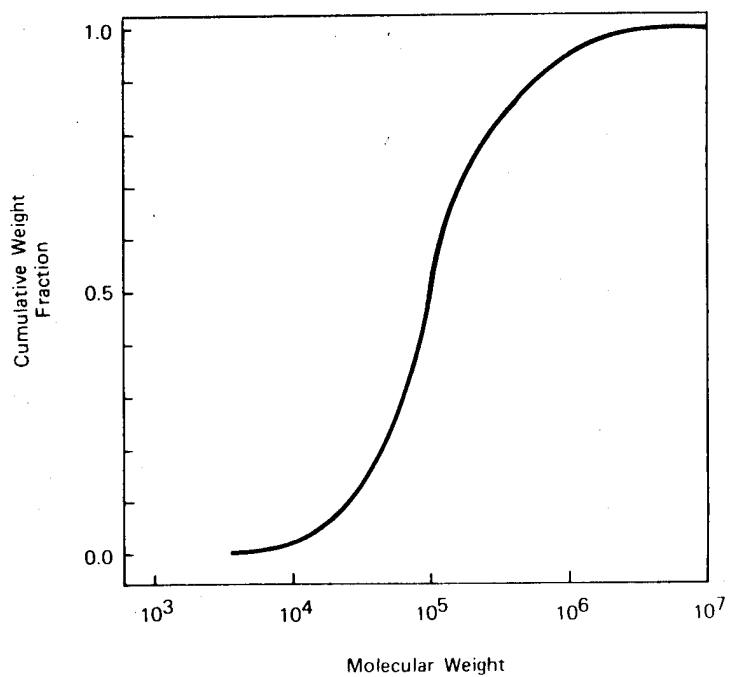
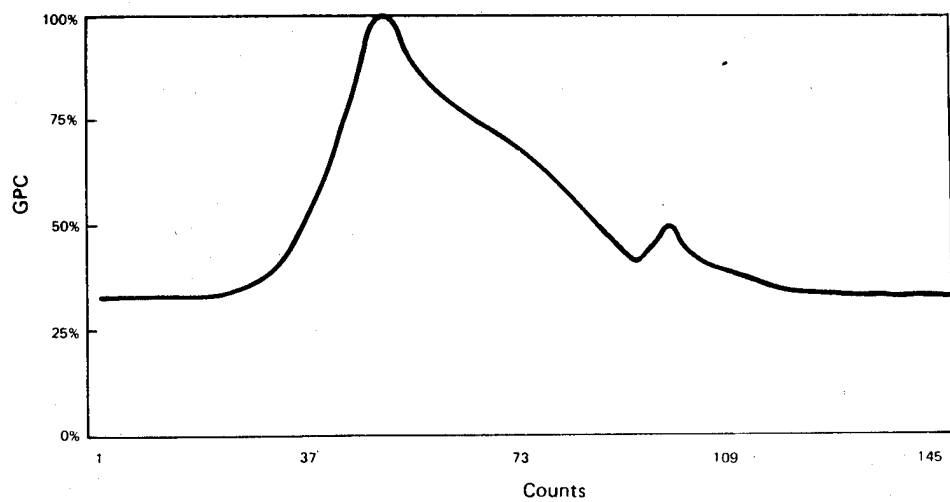


FIGURE 2 - Molecular weight distributions by GPC/LALLS of DAP resin QC-23321 in THF/0.05 wt % maleic acid.

Table 3 - EFFECT OF SOLVENT POLARITY ON DAP "MOLECULAR WEIGHTS"

Solvent System	Polarity Index	$M_w^a$	$M_n^a$	$M_z^a$
THF/0.05% maleic acid	>4.2	336,700	37,800	$3.1 \times 10^6$
Methyl ethyl ketone (MEK)/0.05% maleic acid	4.5 -4.6	172,900	12,200	$1.29 \times 10^6$
MEK/0.05% maleic acid + 0.05M LiBr	>4.6	292,400	19,200	$2.26 \times 10^6$
Dioxane/0.04% maleic acid	>4.8	391,000	38,000	$2.04 \times 10^6$
Dimethyl formamide (DMF)/0.04M LiBr	>6.4	422,000	298,000	$4.0 \times 10^6$
Hexafluoroisopropanol (HFIP)/0.08% NATFAT <sup>b</sup>	>9.3	full associated (single peak) $M_w$ not determined		

<sup>a</sup> Estimated refractive index increment  $dn/dc$  used for molecular weight calculations based on measured value of 0.116 in THF/0.05% maleic acid.

<sup>b</sup> sodium trifluoroacetate.

Table 4 - A COMPARISON OF MOLECULAR WEIGHT DISTRIBUTIONS WITH MOLDABILITY FOR DAP MOLDING RESINS

Program	Resin QC No.	Mol Wt Distributions		Moldability Results
		$M_w/M_n$	$M_z/M_n$	
A	23322	1.6	5.7	Excellent-First choice (transfer molding process)
A	23321	4.3	21	Very Good-Alternate (used for production of another component)
A	23333	No data obtainable		Poor-<50% Acceptable Parts
B	23396	9.1	40	Very Good-Production Resin
C	23553	9.7	101	Very Good-Production Resin
D and E	23531	19.7	185	Good-Production Resin (with a modification of the molding parameters for one component)

was a close second choice and was selected for production in another program. Another Program A candidate resin failed the moldability test; no data on molecular weights or distributions could be obtained for it, because of its partial insolubility (indicating some crosslinking of the prepolymer had already occurred). It is not surprising, therefore, that >50% of the parts molded from it were unacceptable (i.e., had cracks and voids).

For two other molded parts (Programs B and C), DAP resins having  $\sim 10/1 M_w/M_n$  distribution ratios gave good moldability results and were chosen for production. Interestingly, one is a short-glass resin (Program B) and one a long-glass resin (Program C).

The final resin listed in Table 4 was selected for production in Programs D and E, but no alternates for moldability

comparisons were available when it was chosen (as had been the case with the other resins). It gave satisfactory results when molded, but some alterations of molding parameters were required for one component. Its  $M_w/M_n$  ratio of  $\sim 20/1$  probably represents about the upper limit of useful molecular weight distribution ratios and could be too high in some more difficult-to-mold configurations.

In terms of what the high versus low  $M_w/M_n$  molecular weight distribution ratios may mean in relation to the DAP polymer structure, there are two prime possibilities in light of its known polymerization mechanisms: (1) that additional internal cyclization of the *o*-DAP is occurring, or (2) that crosslinking or network structure formation is beginning. The latter would soon result in gel formation and resin insolubility, and is probably the reason that one of the resins tested (QC-23333) could not be completely solubilized. The first reaction, however, would not result in insolubility, but would give an increasingly branched prepolymer structure. This generally increases the  $M_w/M_n$  ratios observed. Also, a continuation of this type of reaction would be expected to produce a less desirable molding resin, as fewer allyl double bonds needed for good fiber-glass adhesion and network structure formation on molding would be available.

Thus, SEC/LALLS helps provide a useful picture of what may constitute a desirable DAP molding resin. However, its drawbacks, in terms of the solvent association effects observed and the lack of absolute molecular weight data, preclude its use as a routine quality control type tool. As a comparative research tool it could be valuable, for example, in studying changes in DAP polymer structure on aging.

## 2.2. Characterization by DSC

A second method used to study and characterize the glass-filled DAP molding resins was differential scanning calorimetry (DSC). DSC has been used extensively in studying heats of reaction of thermosetting resins, such as epoxies [4], and as a quality control analysis tool [5]. It has also been found useful for correlations with resin moldability (in particular, for injection molding applications) of *o*-DAP itself [6]. The relative speed and ease of this type of analysis makes it particularly attractive. It was, therefore, investigated for use here, both to establish a possible relationship to moldability and to monitor changes in the resins on aging, thus determining storage life limits.

### 2.2.1. DSC OF HEAT-AGED RESINS

In order to assess fairly rapidly the potential utility of DSC analysis for the vendor-supplied, glass-filled DAP resins, two were selected and artificially "heat aged" for 1 mo at 120°F. The heats of reaction ( $\Delta H_R$ ) were then determined by DSC and compared to the original resins, which had been kept refrigerated. Results are given in Table 5.

As shown, the two resins tested differed in filler contents, which accounts for the differences observed in heats of reaction of the refrigerated resin samples. What is most significant is that the  $\Delta H_R$  differences between the heat aged and the refrigerated samples, though not large, are detectable by the DSC. (The instrument used for this portion of the work, a Perkin-Elmer DSC-2, is a sensitive research type instrument; the experimental conditions used are given in Table 5). Also, the loss in  $\Delta H_R$  upon artificial heat aging

Table 5 - EFFECT OF HEAT AGING ON HEATS OF REACTION VALUES FOR DAP MOLDING RESINS

Resin QC No.	Filler Content <sup>a</sup> (%)	Storage Conditions	DSC Analyses - Results	
			$\Delta H_R^b$ (cal/g)	$\Delta H_R$ (% change)
23322	63	Refrigerated - Control	13.9 (+3.5%)	
23322	63	Heat Aged 1 mo/120°F	12.6 (+0.6%)	- 9.2
23333	53	Refrigerated - Control	17.9 (+1.7%)	
23333	53	Heat Aged 1 mo/120°F.	15.6 (+2.1%)	-12.8

DSC-2 Conditions: 10°C/min heating rate, 5 mcal/sec range, Indium calibration standard = 6.770 cal/g ( $\Delta H_f$ ).

DSC Pellet Preparation: DAP resin granules ground 10 sec in Wig-L-Bug, pressed into 1/4-in. diam pellets in a 5000-lb-force Carver Press; pellet weights = 16 to 25 mg each.

<sup>a</sup>From analysis for wt % ash content.

<sup>b</sup> $\Delta H_R$  values as calculated are averages of 2-3 separate runs/sample, with deviations as shown.

shows what effects could be expected under adverse storage conditions. The time/temperature chosen, 1 mo/120°F, is not unrealistic in terms of possible shipment and/or storage conditions encountered in summer. All vendor-supplied DAP molding resins are, of course, refrigerated upon receipt at Mound. The utility of DSC analysis for monitoring adverse changes on storage, by determining losses in  $\Delta H_R$ , was therefore demonstrated. This is important as it provides a means for setting realistic storage life limits for the DAP molding resins.

#### 2.2.2. CORRELATION OF DSC ANALYSES WITH MOLDABILITY

Also of interest was the possibility of using DSC analysis to characterize the vendor-supplied, glass-filled DAP resins in relation to their moldability. If

feasible, this could save the considerable time and effort required to complete moldability and physical tests on resins not likely to be suitable for production. The fact that such a correlation had been mentioned in the literature for injection moldable DAP resins was encouraging [6].

##### 2.2.2.1. DSC Peak Moments vs. Moldability

Initially, then, the analysis method developed by Ellerstein [7] and used by Slysh and Guyler for DAP resins [6] was examined here for use with the glass-filled DAP molding resins. In this method, four "moments" of the DSC reaction peak were calculated according to the following equation, as given by Ellerstein:

$$M_n = \frac{\sum_i T_i^n \cdot f_i}{\sum_i f_i} \quad (1)$$

where  $T_i$  is the temperature along the  $i$ th interval along the x-axis of the thermogram, and  $f_i$  is the corresponding height of the curve at that point. The first moment ( $n=1$ ) is the center of gravity of the peak, the second the variance, the third (skewness) is related to peak asymmetry, and the fourth (kurtosis) to the flatness of the curve. Slysh and Guyler found that the centers of gravity for "good" injection molding DAP resins occurred at a higher temperature ( $\geq 168^\circ\text{C}$ ) and that skewness values were positive for the "good" resins, but negative for the "poor" ones (which did not fill mold cavities as well at the molding temperature of  $160^\circ\text{C}$ ).

A computer program, based on one supplied by Ellerstein, was written to permit calculation of these four moments of the DSC reaction peak for the DAP resin. A PDP-12 computer was used, which was interfaced with the Perkin-Elmer DSC-1B instrument used for the DSC analyses. DSC instrument conditions are given in Table 6. Resin pellets of  $\sim 27$  mg were prepared for analysis, according to the method of Willard [8]. The initial results obtained are given in Table 7, along with a designation of the DAP resin as "acceptable" or "not acceptable" in moldability, depending on whether it gave  $\geq 50\%$  acceptable molded parts. (This is simply our arbitrary designation -- obviously, acceptance rates much higher than 50% would be desired in production).

Inspection of the results in Table 7 does not reveal any consistent trend or pattern of DSC peak moments vs. the moldability. Three factors may be involved here: (1) differences in types of molding operations used, i.e., injection molding (literature) vs. transfer/compression molding

(Mound); (2) differences in the parts to be molded themselves; and (3) inherent lack of reproducibility due to limitations of the instrumentation. Thus, what might be useful as criteria for moldability for one plastic part or type of molding operation may not apply to another. For example, the Program A molded part is a thin, spherical disc; the Program B part is larger and cylindrical. However, even for Program A, with the four resins tested, there is no consistent pattern observed for the DSC moment values in the "acceptable" vs. "not acceptable" molding resins. Therefore, this method of DSC analysis was not considered sufficiently useful or reproducible to warrant a continuation of its use with the instrumentation available at this time.

#### 2.2.2.2. DSC Heats of Reaction of DAP Resins vs. Moldability

Even though the calculated moments of the DSC peaks did not appear to correlate well with the moldability of the DAP resins, it was still considered quite possible that the DSC heat of reaction ( $\Delta H_R$ ) data, combined with other analyses, could provide such a correlation.

Since the molding resins all contained at least 50% filler (primarily fiberglass), the  $\Delta H_R$  values for these resins should vary inversely as a function of the filler content in a nearly straight line relationship. This presumes, of course, that all have processed to about the same stage of reaction prior to molding, and that the fillers (other than fiberglass), catalysts, and inhibitors used are nearly the same. Obviously, such is not necessarily the case with resins supplied by different vendors, and therefore differences in  $\Delta H_R$  vs. percentage of filler could indeed be observed among them.

Table 6 - DSC HEAT OF REACTION DATA VS. MOLDABILITY OF GLASS-FILLED DAP RESINS

DAP Resin Identification				Rheometer Minimum Torque (in./lb)	Filler (wt %) <sup>a</sup>	$\Delta H_R$ by DSC (cal/g)	Moldability <sup>b</sup>
Program	Vendor	Type	QC No.				
A	Allied	Short Glass, Blue	23322 <sup>c</sup>	13	62.8	13.1 (+ 1.9)	Acceptable
	Allied	Same	23321	16	62.4	13.5 (+ 2.0)	Acceptable
	Allied	Same	23272	27	60.7	11.5 (+ 1.7)	Not Acceptable
	Allied	Same	23273	13	60.9	14.4 (+ 2.2)	Acceptable
	USP	Same	23333	No min.	52.5	15.3 (+ 2.3)	Not Acceptable
	USP	Same	23334	No min.	52.3	18.4 (+ 2.8)	Acceptable
B	USP	Short Glass, Green	23396 <sup>c</sup>	9	59.9	14.6 (+ 2.2)	Acceptable
	USP	Same	23395	15	68.5	10.5 (+ 1.6)	Not Moldable
	Allied	Same	24117	7.5	62.5	14.9 (+ 2.2)	--
	Allied	Same	24116	5.5	63.2	14.1 (+ 2.1)	--
C	Allied	Long Glass, Green	23553 <sup>c</sup>	5.5	54.2	18.3 (+ 2.7)	Acceptable
	Allied	Same	23552	7.5	54.5	15.1 (+ 2.3)	Not Acceptable
D and E	USP	Short Glass, Blue	23531 <sup>c</sup>	8	52.9	13.5 (+ 2.0)	--
	Allied	Same	24118	9	62.6	14.3 (+ 2.1)	--

DSC-1B conditions

Sample Size: ~27 mg, pelletized at 5 KPSI

Ordinate Sensitivity: 16 mcal/sec (full scale)

Scan Rate: 20°C/min

Purge: N<sub>2</sub> at 10 cm<sup>3</sup>/min

Daily duplicate ordinate/abscissa calibrations were performed prior to sample analysis.

<sup>a</sup>As determined by ash content.<sup>b</sup>Acceptable means  $\geq 50\%$  of molded parts rated acceptable; not acceptable means  $\leq 50\%$  of parts rated acceptable.<sup>c</sup>Resins used in production of these components.

Table 7 - DSC PEAK MOMENTS VS. MOLDABILITY OF GLASS-FILLED DAP RESINS

Program	Resin QC No.	Moments of DSC Peak <sup>a</sup>			Moldability <sup>b</sup>
		Center of Gravity (°C)	Skewness	Kurtosis	
A	23322	166	0.14	1.48	Acceptable
	23321	166	0.21, 0.60	1.64	Acceptable
	23272	167	0.24	1.52	Not Acceptable
	23333	160	0.0004, -0.01	1.38	Not Acceptable
B	23396	156	0.04	1.39	Acceptable
	23395	165	0.36	1.60	Not Moldable (69% filler)
C	23553	167	0.22, 0.31	1.61	Acceptable
	23552	165	0.24	1.59	Not Acceptable

See Table 6 for DSC conditions used.

<sup>a</sup>Values given are averages of two, except where very far apart; then individual values are shown.

<sup>b</sup>Acceptable means  $\geq 50\%$  molded parts rated acceptable;  
not acceptable means  $< 50\%$  of molded parts rated acceptable.

Table 6 identifies the different glass-filled DAP resins according to vendor, program, type and weight percent of ash (filler) content, and gives the results of rheometer minimum torque (in./lb), which is an indication of resin flow, as well as the DSC heat of reaction ( $\Delta H_R$ ) data. As shown in Table 6, there does not appear to be any definite correlation between the rheometer minimum torque values and "acceptability" in moldability (as previously defined). Only one resin rated "not acceptable" was also outside the acceptance limits for minimum torque, with a value of 27. Thus, rheometer testing alone would not be sufficient to screen out unacceptable DAP molding resins.

The DSC heat of reaction data cannot be considered alone, but must be correlated with the filler content of the DAP molding resin. It may be noted in Table 6 that

there is some variation in  $\Delta H_R$  observed for resins of the same filler content, and that those with the lower  $\Delta H_R$  values for a given filler content are the ones rated "not acceptable" on moldability.

This trend can be seen graphically in Figure 3, where the DSC  $\Delta H_R$  values are plotted against filler content. The center points (or average of two  $\Delta H_R$  values) are used in the plot, but, with the DSC-1B instrument employed for this work,  $\pm 15\%$  is the observed statistical limit of precision for the analysis. For the resin points marked with a triangle ( $\Delta$ ), the statistical limits of the analysis are drawn in, and a "band" drawn encompassing these limits. It is also possible to draw a straight line through these points, and it should be noted that some of the resins whose center points fall on this line are those being used as production resins.

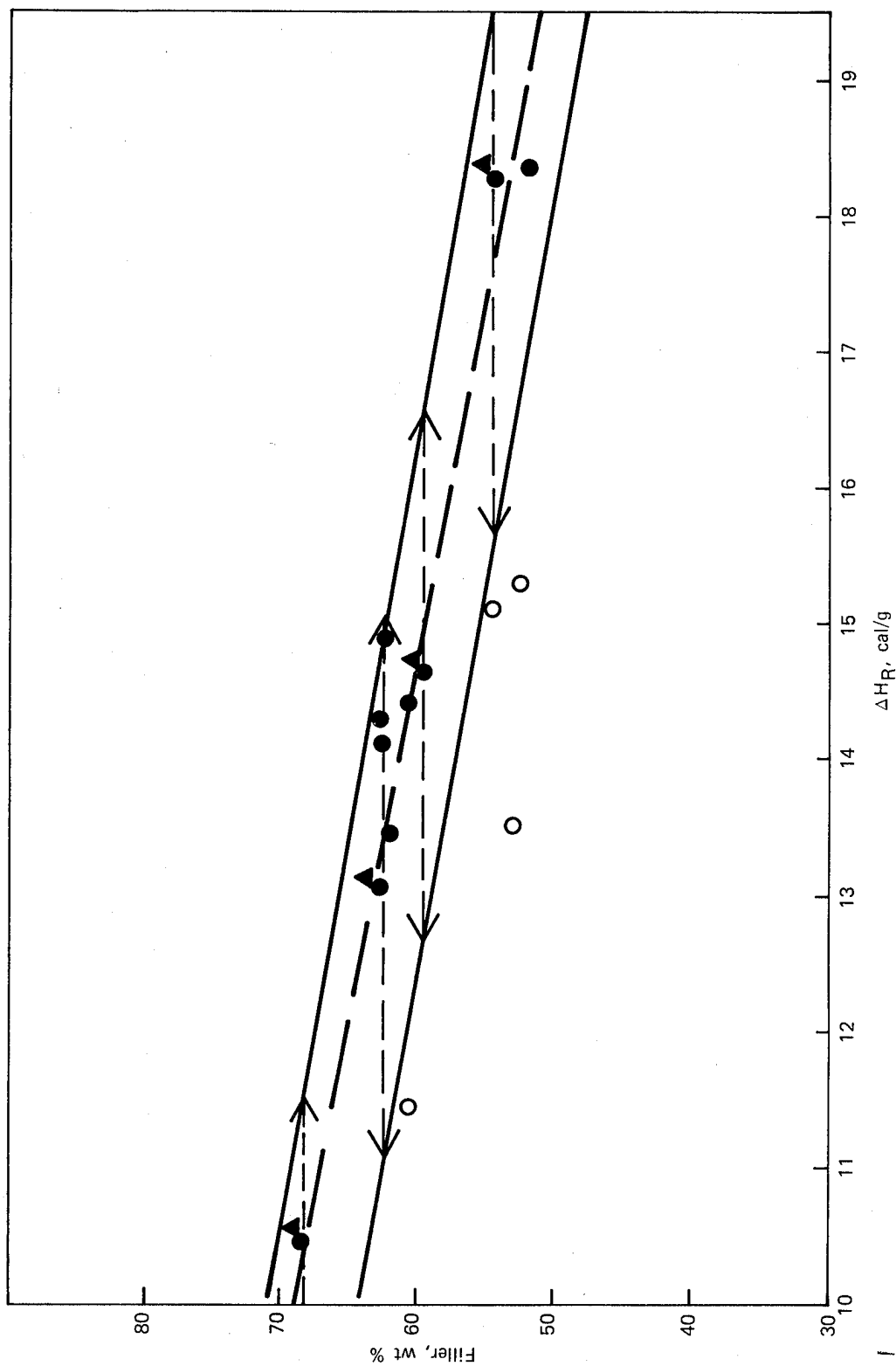


FIGURE 3 - DSC characterization of DAP molding resins. (See text on the previous page for an explanation.)

The others within the band are all rated as "acceptable" in moldability (or may not have been tested yet). One exception is the resin with nearly 70% filler content, which was not moldable; its  $\Delta H_R$  value falls as expected for this filler content, but there is probably too little resin present to give a good molding compound. The circles below the band are the  $\Delta H_R$  center points of other DAP resins, three of which tested unacceptable on moldability, with the fourth exhibiting difficulty in molding.

There are two possible explanations for the lower than expected  $\Delta H_R$  values observed for these DAP molding resins:

(1) the reaction of the DAP prepolymer has proceeded farther than desirable during processing of the molding resin (whether by crosslinking or internal cyclization or both); or (2) there has been some nonre-active organic "filler" or extender added,

such as a less expensive thermoplastic resin. Such a filler assists in flow, but does not contribute to crosslinking or network formation on molding. Resin flow would not be adversely affected (as measured by rheometer or spiral flow measurements) by this second possibility and by the first only if crosslinking were predominating over cyclization of the DAP prepolymer. DSC data alone cannot distinguish between the various possibilities cited.

It is, therefore, of interest to compare both the DSC and GPC results with moldability; this is done in Table 8. Here the DSC results are indicated as "good" or "poor" depending on whether the center points are within or outside the band limits drawn in Figure 3. As shown, Resin QC-23333, which was partially insoluble in the GPC test was also "poor" on DSC and unacceptable in moldability. Both DSC and

Table 8 - CORRELATION OF DSC/GPC RESULTS WITH MOLDABILITY OF DAP RESINS

Program	Resin QC No.	GPC ( $M_w/M_n$ )	DSC Results	Moldability
A	23322	1.6	Good	Production Resin-Transfer Molding
	23321	4.3	Good	Production Resin for another component
	23333	Not obtainable due to resin insolubility	Poor	<50% Acceptable Parts
	23272	---	Poor	<50% Acceptable Parts
	23396	9.1	Good	Production Resin
B	23395	---	Good	Not Moldable (70% filler)
C	23553	9.7	Good	Production Resin
	23552	---	Poor	<50% Acceptable Parts
{ D and E }	23531	19.7	Poor	Production Resin (no alternates available initially)
	24118	---	Good	Not yet determined

GPC test results thus indicate that the DAP crosslinking reaction had proceeded too far in the processing of this molding resin. All other DAP resins with GPC  $M_w/M_n$  ratios of  $\leq 10/1$  were "good" in DSC results and acceptable in moldability. The  $\sim 20/1$   $M_w/M_n$  ratio DAP resin was "poor" in DSC results and, although usable for production, was somewhat difficult to mold in one configuration. The GPC/DSC results on this resin would indicate that while additional internal branching or cyclization of o-DAP has occurred, the crosslinking reaction has not proceed so far that it is no longer soluble or moldable. Thus, the combined GPC and DSC results can be an indication of the types of reactions which have occurred in the preparation of these glass-filled DAP molding resins.

Importantly, DSC heat of reaction data, combined with a determination of percentage of filler content, can be used to predict which vendor-supplied DAP resins have the best potential for high acceptance rates in production of molded parts, and which may cause difficulty in molding or have low acceptance rates, even among DAP molding resins whose rheometer flow rates are all acceptable. Also, the use of improved thermal analytical instrumentation for the quality control analysis of the DAP resins (i.e., of the DSC-2 type as opposed to the DSC-1B used here) should narrow the statistical certainty limits and improve predictions. Thus, DSC determination of DAP resin heats of reaction is a useful quality control tool, both to predict potential moldability and to determine changes in the resin on storage. When combined with other research characterization methods, such as SEC/LALLS, additional insight into the nature of the changes in DAP polymer structure on resin storage or processing can be gained.

### 3. Characterization and completeness of cure of the molded DAP parts

As an adjunct to the characterization of the vendor-supplied, glass-filled DAP molding resins, thermal analysis on the actual parts molded from these resins was performed. This involved DSC determination of completeness of cure of the molded parts (before and after any post-molding "baking" treatments), and also thermomechanical analysis (TMA) determination of the glass transition temperatures ( $T_g$ 's) prior to and after post-curing. The DSC work will be described first, then the TMA work, which verified and helped to explain some of the observed results.

#### 3.1. DSC determination of completeness of cure

##### 3.1.1. EXPERIMENTAL

In all cases, the DAP molded parts that were examined for completeness of cure either were taken from the same groups of parts that were selected for chloroform extraction testing or were the other half of the actual part so tested (as in the case of Program B involving a larger part). It should be noted that all molded parts passed the chloroform extraction test (which involves a measurement of any dimensional changes following a 2-hr Soxhlet extraction of the parts in chloroform). Thus, all parts were acceptable as produced. The effects of two post-curing temperatures (135°C and 165°C) were determined for DAP molded parts (Programs A, B, and C). The instrument employed for all runs was a Perkin-Elmer differential

scanning calorimeter, Model DSC-2, with a scanning rate of 20°C per minute.

The initial DAP molding resin compound (the starting material for each component) and 3-mg pieces broken from the molded parts were all run in loosely covered aluminum pans vs. a loosely covered empty aluminum pan as a reference. All runs were made with argon gas flowing over the DSC head. Paul E. Willard [9] has proposed that the thickness of molded parts will determine to some degree the amount of curing time and temperature required to complete the cure. The poor thermal conductivity of the DAP (combined with the effect of exothermic heat of reaction) will in many cases allow the thick sections to cure faster or more completely than the thin sections. Therefore, pieces from similar thicknesses of the part to be investigated must be used for duplicate comparisons and similar masses used for the DSC runs. As noted by Willard, different results may be obtained on the same parts in areas having different thicknesses.

In Figure 4 the curves for the three runs on the Program C molded part and its starting material are compared. The areas under the curves were integrated using a planimeter and placing these results in the formula:

$$\% \text{ conversion} = \frac{A_o - A}{A_o} \times 100$$

where  $A_o$  = area of the starting material, and  $A$  = the area of the cured part.

### 3.1.2. RESULTS AND DISCUSSION

Figure 4 illustrates results obtained on the Program C molded parts and starting resin, and Table 9 gives the complete results obtained on three molded parts tested.

(In each case more than just one part, and also various sections of the same part, were tested). The post-curing conditions used for each of the molded parts are given in Table 9. DSC results on each type of molded part will be discussed separately, along with their overall implications.

The Program B parts as molded showed no residual DSC curing peak, indicating that 100% cure was obtained on molding. As mentioned, this is the thickest molded part (~1/2-in. diameter cylinder) of those tested, and the exothermic DAP heat of reaction is no doubt a factor in obtaining 100% cure as molded, in accordance with the results cited by Willard [9].

Mixed results were obtained with Program A molded parts (thin discs): in some, cure was complete as molded; others showed a very slight residual curing peak. Perhaps very slight differences in molding conditions are responsible for these differences. Some of the Program A parts were post-cured (2 hr/165°C) and these were all 100% cured. However, since no measurement of completeness of cure was made on these same parts before post-curing, it cannot be ascertained whether or not they were completely cured on molding.

Much more definitive results were obtained with the thicker Program C molded parts. The "as-molded" parts were 95% cured, and essentially the same DSC curve obtained for these as shown in Figure 4 for the 2 hr/135°C post-cured sample. The two post-cure conditions tested were: 2 hr/135°C and 2 hr/165°C. As shown in Figure 4 and Table 9, the latter conditions were effective in completing the cure, whereas

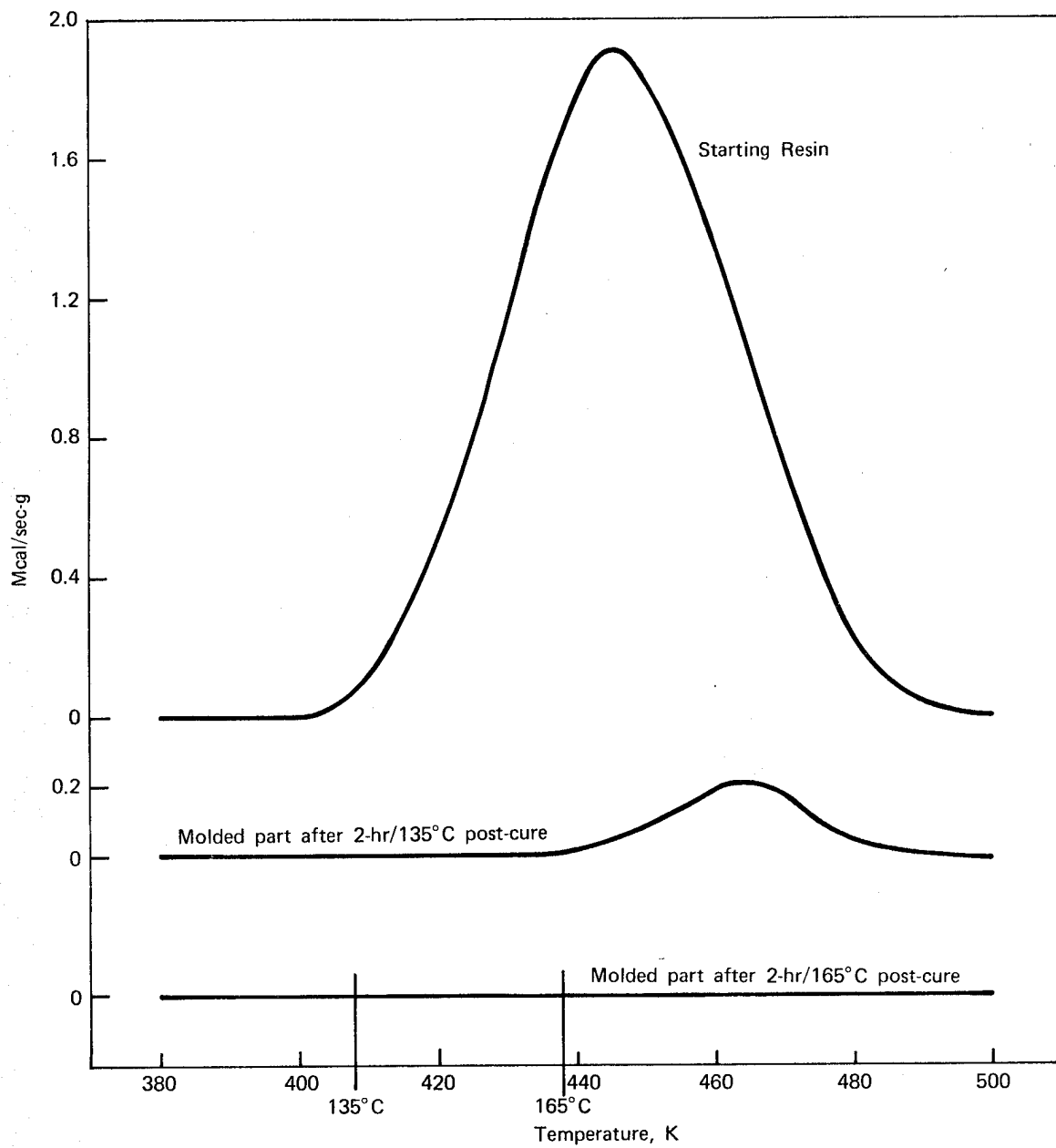


FIGURE 4 - DSC curves of DAP resin and molded Program C parts.

Table 9 - COMPLETENESS OF CURE OF DAP MOLDED PARTS

Program No.	Post-Cure of Molded Parts	CHCl <sub>3</sub> Extraction Test	DSC % Cure	TMA T <sub>g</sub> (°C)
A	None	Pass	Some = 100 Some < 100	155 - 65 140 - 45
A	2-hr/165°C	----	100	155 - 65
C	None	Pass	95	---
C	2-hr/135°C	----	95	---
C	2-hr/165°C	----	100	---
B	None	Pass	100	---

the former were not. The reasons for this will be discussed in connection with the TMA results obtained on the Program A parts. In terms of part geometries, the Program C part is intermediate in thickness between those of Programs A and B. It is apparently not so thick that the reaction exotherm is sufficient to complete the cure on molding, but thick enough that the poor thermal conductivity of DAP is a factor.

### 3.2. TMA determination of T<sub>g</sub>'s

In addition to DSC, thermomechanical analysis (TMA) of DAP molded parts was performed, both to determine the actual glass transition (T<sub>g</sub>) of the cured DAP resin and to confirm the DSC results. The T<sub>g</sub> of a thermosetting resin is known to increase with increasing degree of cure or polymerization until the final or ultimate T<sub>g</sub> of the resin is reached [10]. Thus, it provides another method for determining completeness of cure of a molded part.

#### 3.2.1. EXPERIMENTAL

The TMA used was a DuPont 943 Thermomechanical Analyzer, interfaced with the DuPont 990 Programmer/Plotter. Unless otherwise noted, all experiments were conducted using the expansion probe. In general,

conditions employed were: 10°C/min heating rate, 5-g load, range settings of Y=0.1 and Y=0.2 mil/in. (dY mode), 2 min/in. time base. For the experiments with the penetration probe, 10- and 20-g loads were used. Scans were from ~25 to ~200°C.

The samples were small, flat pieces from the molded parts. The Program A molded part was particularly well suited for this analysis because of its thin, flat configuration. Hence, all initial work was performed using it. It should be noted that due to the high filler content (50-60%), glass transitions are not as easy to detect as in a pure resin, using TMA.

#### 3.2.2. RESULTS

Typical results obtained for the TMA runs on the Program A parts, using the expansion probe, are shown in Figure 5. The sample from a Program A molded part with no post-cure after molding initially exhibited a T<sub>g</sub> of ~143°C. When the same sample was re-run, the T<sub>g</sub> had increased to ~163°C. This increase in T<sub>g</sub> indicates that the as-molded sample was not 100% cured. Additional curing occurred during the first TMA run itself, and the T<sub>g</sub> on the second run of this sample was ~20°C higher. This same phenomenon was observed with different

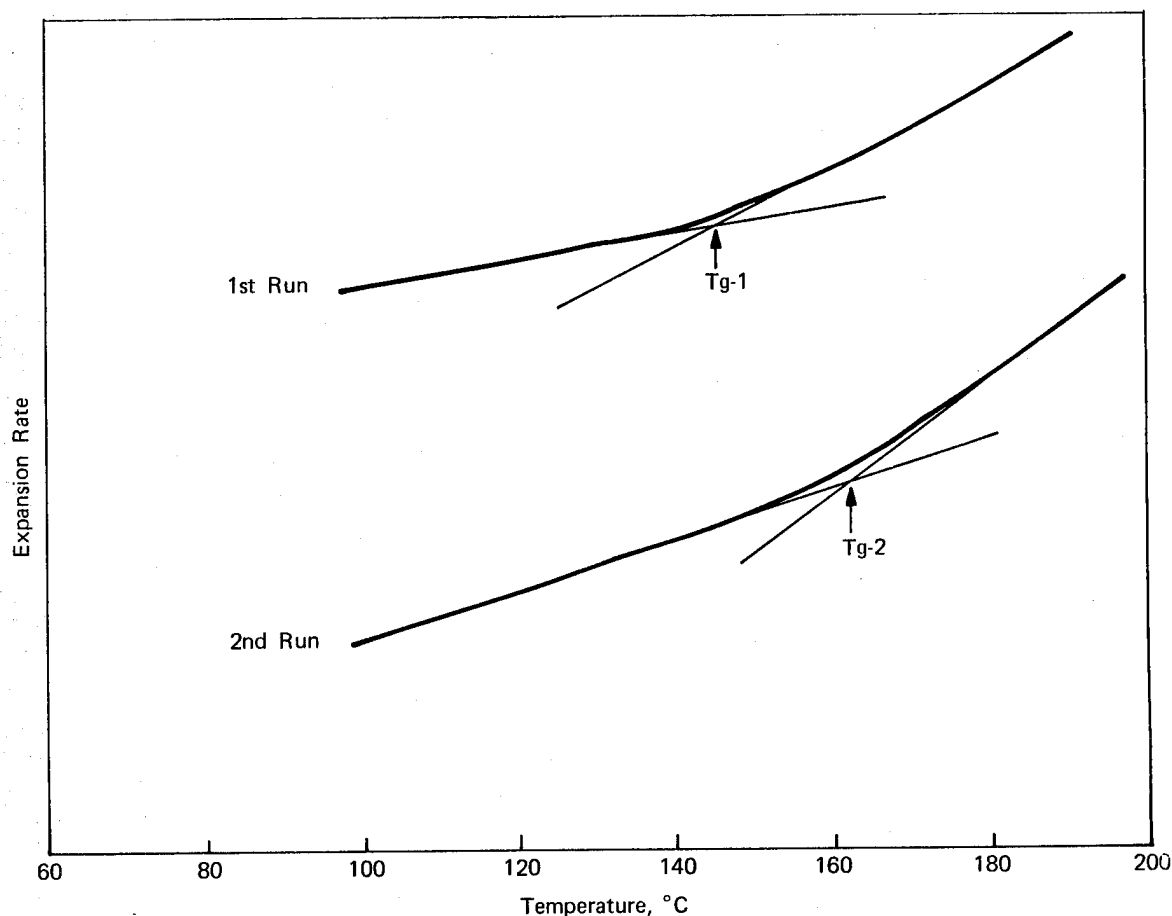


FIGURE 5 -  $T_g$ 's of molded DAP parts (Program A) by TMA.

Program A molded parts, and with pieces taken from different portions of the same Program A molded part (i.e., edges, centers, etc). However, some of the as-molded parts exhibited  $T_g$ 's of  $\sim 155$ - $65^\circ\text{C}$ , indicating they were nearly 100% cured as molded (this also verifies the DSC results in which some of the as-molded Program A parts did not exhibit any residual curing peaks). As expected, the 2 hr/ $165^\circ\text{C}$  post-cured molded parts appeared completely cured, by both TMA and DSC. However, it could not be determined whether they were 100% cured by initial molding or by the post-curing operation.

$T_g$ 's of  $\sim 160$ - $165^\circ\text{C}$  were observed by TMA, with  $165^\circ\text{C}$  representing the ultimate  $T_{g\infty}$  ( $T_g$  at complete cure) of this o-DAP resin.

This subsequently was confirmed by a dynamic mechanical analysis scan (on a DuPont 1090/980 DMA) of a Program A molded part, post-cured 2 hr/ $165^\circ\text{C}$ , in which the damping peak corresponding to  $T_g$  occurred at  $165^\circ\text{C}$ .

Table 9 gives a summary of both the DSC and the TMA results on all the DAP molded parts included in this study. Of particular importance is the fact that all the molded DAP parts passed the chloroform extraction tests, including those which were identified as less than 100% cured by DSC or TMA. Also, in a TMA experiment on an as-molded Program A part using the penetration probe, no "softening" (or down turning of the TMA curve) was observed at  $T_g$  (as is the case with elastomers). Instead a continued upward expansion was obtained, which verified the hardness of the molded DAP parts, even if they were not 100% cured.

The conclusion from both the DSC and TMA work is that any post-curing operation which may be performed on DAP molded parts, with the objective of achieving 100% cure, must be conducted at  $\geq 165^{\circ}\text{C}$ . Furthermore, these results are consistent with an established model of network polymer formation (Figure 6), as developed by J. K. Gillham [11]. In this model, it is stated that if the reaction ceases at vitrification (where  $T_{\text{cure}} < T_{g\infty}$ ), the glass transition temperature,  $T_g$ , of the system after cure will equal the temperature of cure. Importantly, if  $T_{\text{cure}} < T_{g\infty}$ , the material will have to be post-cured above  $T_{g\infty}$  to achieve a complete cure. Since  $T_{g\infty}$  has been demonstrated here to be  $\sim 165^{\circ}\text{C}$  for a fully cured DAP polymer, it is evident that any post-curing operations must be conducted at  $\geq 165^{\circ}\text{C}$  to achieve 100% cure. Longer times at lower temperatures will not produce equivalent results.

One other aspect of this model (see Figure 6) is also important in regard to storage conditions for the DAP prepolymer resins. It states that if the storage temperature is below  $T_{gg}$  ( $T_g$  at gelation), a reactive material will convert to a vitrified solid of low molecular weight, which is stable and can later be liquefied by heat and processed. However, above  $T_{gg}$  the storage life of the resin is finite since gelation will occur before vitrification. The  $T_{gg}$  for DAP prepolymers has not as yet been defined, but preliminary indications from some of the TMA thermograms of the molded parts are that it is in the range of  $\sim 60$ – $80^{\circ}\text{C}$ . Thus, continuous storage of DAP molding resins well below these temperatures is mandatory for extended shelf life to be obtained. Further investigation is warranted, particularly an accurate determination of  $T_{gg}$  for the DAP molding resins.

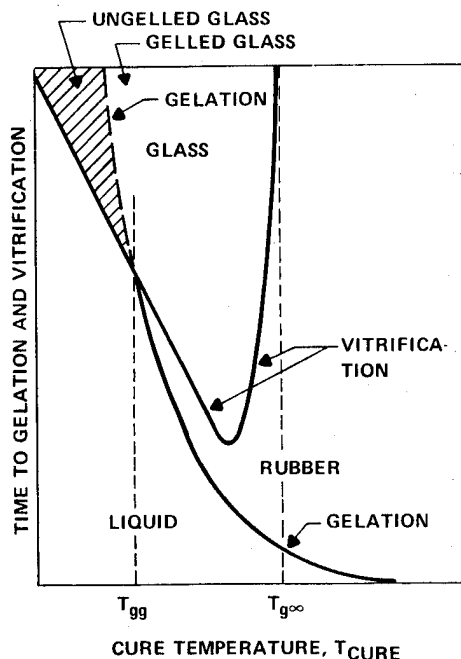


FIGURE 6 - Time to gel and time to vitrify vs isothermal cure temperature for an epoxy system.  $T_{gg}$  and  $T_{g\infty}$  are critical temperatures in the phase diagram which shows the four states of materials encountered in the thermo-setting process, i.e., liquid, rubber, ungelled glass, and gelled glass. [Ref. 11]

In conclusion then, with the use of some of the characterization techniques outlined in this report, it is possible that both the moldability and the storage life limits of a DAP prepolymer molding resin can be predicted and controlled.

## 4. Future work

While the initial results obtained in this study were encouraging in terms of developing characterization methods with potential for predicting both moldability and storage life limits for DAP molding resins, a continuation of this work is needed to verify these results. Some of the planned or suggested future work on DAP is outlined in this section.

## 4.1. DSC/TMA analyses of DAP resins

To further verify the method suggested here for predicting moldability of DAP resins by DSC analysis, monitoring of all incoming vendor-supplied (or in-house produced), glass-filled DAP resins should be continued. Further, retesting by DSC of all resins (or at least those accepted as suitable for production purposes) should be done at regular (i.e.,  $\approx 6$  month) intervals to ensure that no large ( $\geq 20\%$ ) decrease in heats of reaction have occurred upon storage. By developing such a data base on a fairly large number of resins, reasonable storage life limits can then be set. TMA determination of the  $T_g$  of the DAP resins before molding would assist by verifying the storage temperature limits below which the DAP resin should be stored continuously.

## 4.2. Other characterization methods for DAP resins

There are a number of other analytical or characterization methods for DAP which have not yet been examined and which do have potential for utility with these molding resins, and with cured or molded parts. The three listed below are good possibilities, but any actual work with them in the future will depend on time, funds, and instrument availability. (1) Dynamic Mechanical Analysis (DMA) is a method used to study cure characteristics, secondary transitions, such as  $T_g$ , and relationships to physical properties, such as impact strength, of polymers. It is particularly useful for filled and thermosetting resins [12]. (2) Fourier Transform Nuclear Magnetic Resonance (FTNMR), particularly

solid-state, could be useful in determining more accurately the nature of the reactions occurring as the DAP resin "ages" on storage or as it is cured by heating on processing or molding (i.e., internal cyclization, branching, network formation, etc). (3) Since the vendor-supplied DAP molding resins are all mixtures of several components (prepolymer, monomer, filler, catalyst, inhibitor, mold release agent, pigment, etc.), if a more definite identification of these components is desired, Infrared (IR) Difference Spectra would be useful. This would require a spectral library with the individual component spectra in it, however. Separation of some of the low molecular weight components (i.e., by gas or liquid chromatography) may also be possible followed by identification with IR. A better understanding of the nature of vendor-supplied DAP molding resins may help not only in determining their utility and storage life expectancy, but also in guiding any future development of in-house production of fiberglass-filled DAP molding resins.

## 5. Acknowledgements

The authors would like to acknowledge the contributions of the following individuals toward this work: Dr. A. S. Kenyon and Dr. J. D. Wellons for helpful discussions on the SEC/LALLS work; D. E. Etter for the DSC data on heat-aged DAP resins; Dr. S. M. Ellerstein (Thiokol Chemical Corp.) for providing the computer program on DSC peak moments and A. F. Ciramella for its adaptation to instrumentation at Mound; and the Mound Analytical and Manufacturing Development Sections for providing other relevant data cited here.

## 6. References

1. W. Simpson, T. Holt, and R. J. Zetie, J. Polym. Sci., 10, 489 (1953).
2. W. Simpson and T. Holt, Proc. Royal Soc. (London), A238, 154 (1956).
3. R. Slysh, et al, Polym. Eng. Sci., 14, 264 (1974).
4. R. Botham, M. Bank, R. Bayless, and P. Shank, Mod. Plast., Nov. 1973, p. 84.
5. Plast. World, Aug. 1979, p. 69.
6. R. Slysh and K. E. Guyler, Polym. Eng. Sci., 18, 607 (1978).
7. S. M. Ellerstein, Anal. Calorimetry, 2, 389 (1968).
8. P. E. Willard, J. Macromol. Sci. - Chem., A8(1), 33 (1974).
9. P. E. Willard, Insul. Circuits, 18, 17 (October 1972).
10. F. Bueche, "Physical Properties of Polymers," p. 113, J. Wiley and Sons, New York, 1962.
11. J. K. Gillham, Polym. Eng. Sci., 19, 676 (1979).
12. R. L. Hassel, Industrial Research/Development, 20(10), 160 (1978).

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